(19) World Intellectual Property Organization International Bureau



E CERTO CONTRER DO CORROS CORROS COMO DE CORRES ENTO A COMO DE COMO DECUDA DO COMO PARA FORMA COMO DE COMO DECU

(43) International Publication Date 26 January 2006 (26.01.2006)

(10) International Publication Number WO 2006/008659 A2

(51) International Patent Classification:

Not classified

(21) International Application Number:

PCT/IB2005/003176

(22) International Filing Date: 25 July 2005 (25.07.2005)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 10/897,844

23 July 2004 (23.07.2004) US

(71) Applicants (for all designated States except US): FEDERAL MOGUL IGNITION COMPANY (UK) LIMITED [GB/GB]; Arrowbrook Road, Upton Wirral, Merseyside, L49 0UQ (GB). JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1 5B (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): TINWELL, Paul [GB/FR]; 23 St. Catherines Drive, Hartford, Northwich, Chesire CW8 2FE (GB). ORJELA, Gurdev [BE/BE]; 56, Rue de l'Eau, Autelbas Barnich, B-6700 ARLON (BE). HYDE, Robin [GB/GB]; 5 Wilbury Close, Letchworth, Hertfordshire SG6 4JX (GB). COUPLAND, Duncan, R.

[GB/GB]; 68 Warren Wood Drive, High Wycombe, Bucks HP11 1 EA (GB).

- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

 without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: IGNITION DEVICE HAVING AN ELECTRODE TIP FORMED FROM AN IRIDIUM-BASED ALLOY

(57) Abstract: An ignition device such as a spark plug (10) having center and ground electrodes (16, 18), at least one of which includes a firing tip (20, 22) formed from an alloy containing iridium, rhodium, tungsten, and zirconium. With the inclusion of tungsten and zirconium in the alloy, the percentage of rhodium can be kept relatively low without sacrificing the erosion resistance or reduced sparking voltage of the firing tip. In one embodiment, the firing tip (20, 22) contains 2 wt % rhodium, 0.3 wt tungsten, 0.02 wt % zirconium, and the balance iridium.



WO 2006/008659 PCT/IB2005/003176

IGNITION DEVICE HAVING AN ELECTRODE TIP FORMED FROM AN IRIDIUM-BASED ALLOY

TECHNICAL FIELD

5

10

15

20

25

30

This invention relates generally to spark plugs and other ignition devices used in internal combustion engines and, more particularly, to such ignition devices having noble metal firing tips. As used herein, the term "ignition device" means spark plugs, igniters, and other such devices that are used to initiate the combustion of a gas or fuel.

BACKGROUND OF THE INVENTION

A variety of iridium-based alloys have been proposed for use in spark plug electrodes to increase the erosion resistance of the firing surfaces of the electrodes. Iridium-based alloys typically have a relatively high melting point and are more resistant to spark erosion than many of the metals widely used today. The iridium-based alloy is typically used in the form of a pad or rivet that is laser welded or otherwise metallurgically bonded to the center and ground electrodes on either side of the spark gap. There are, however, known disadvantages to the use of certain iridium-based alloys, including difficulty in bonding that material to the electrodes and oxidative volatilization of the alloy at higher temperatures. The present invention addresses the latter of these two problems.

A known approach for reducing the oxidative loss of iridium is to utilize it in the form of an alloy combined with rhodium. U.S. Patent No. 6,094,000 and published UK patent application GB 2,302,367 to Osamura et al. discloses such an alloy in which rhodium can be included in an amount ranging from 1-60 wt %. Oxides of group 3A and 4A elements such as yttria or zirconia can also be added to help reduce consumption resistance. Notwithstanding Osamura et al.'s teaching of use of rhodium in amounts as low as 1%, it has been found that minimization of oxidative loss of the iridium at higher temperatures requires much higher amounts of rhodium. This is borne out in the test data presented by Osamura et al. and their patent notes that the amount of rhodium is preferably at least 3%.

10

15

20

25

30

U.S. Patent No. 5,793,793 to Matsutani et al. reports a similar finding, wherein the amount of rhodium is kept within the range of 3-50 wt % and, most preferably, is at least 18 %. In U.S. Patent No. 5,998,913, Matsutani identifies some disadvantages of the inclusion of high percentages of rhodium and, in an effort to reduce the amount of rhodium in the alloy, proposes the addition of rhenium or ruthenium. According to this patent, by adding rhenium and/or ruthenium in amounts up to 17 wt %, the amount of rhodium needed to maintain good resistance to oxidative consumption can be lowered to as little as 0.1 wt %.

The inventors have discovered that an iridium alloy containing rhodium, tungsten, and zirconium permits the use of lower amounts of rhodium while maintaining good erosion resistance and lowered sparking voltages. See WO 2004/007782A1 and WO 2004/008596A2, both published January 22, 2004. In WO 2004/007782A1, an iridium based alloy for spark plug electrodes is disclosed in which the alloy can contain 0.1-5 wt % rhodium, 0.01-5 wt % tungsten, and 0.01-0.5 wt % zirconium. In addition to these broad ranges of elements, this published application includes a specific example of this which includes 2.5 wt % rhodium, 0.3 wt % tungsten, and 0.07 wt % zirconium. WO 2004/008596A2 also discloses this particular formulation with slightly broadened ranges of 1-3 wt % rhodium, 0.1-0.5 wt % tungsten, and 0.05-0.1 wt % zirconium.

SUMMARY OF THE INVENTION

The present invention is directed to an ignition device having a pair of electrodes defining a spark gap therebetween, with at least one of the electrodes including a firing tip formed from an alloy of iridium, rhodium, tungsten, and zirconium, in which the zirconium is held below 0.05 wt % and is preferably about 0.02 wt % when the amount of tungsten is held at 0.3 wt % and the amount of rhodium is reduced to about 2 wt %. The inventors have discovered that the reduction of rhodium content to 2 wt % along with the reduction of zirconium to 0.02 wt % surprising yields better overall results than the specific formulations disclosed in their prior applications noted above. These unexpected results include better workability of the alloy when forming it into small diameter (e.g., 0.7 mm) electrode wires as well as

10

15

20

25

spark plug operational performance that is as good as or marginally better than the prior specific formulations.

BRIEF DESCRIPTION OF THE DRAWINGS

A preferred exemplary embodiment of the present invention will hereinafter be described in conjunction with the appended drawings, wherein like designations denote like elements, and:

Figure 1 is a fragmentary view and a partially cross-sectional view of a spark plug constructed in accordance with a preferred embodiment of the invention;

Figure 2 is a side view of a rivet that can be used in place of the firing tip pads used on the spark plug of Fig. 1; and

Figure 3 depicts a wire that can be used in place of the firing tip pads shown in Fig. 1.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to Fig. 1, there is shown the working end of a spark plug 10 that includes a metal casing or housing 12, an insulator 14 secured within the housing, a center electrode 16, a ground electrode 18, and a pair of firing tips 20, 22 located opposite each other on the center and ground electrodes 16, 18, respectively. Housing 12 can be constructed in a conventional manner and can include standard threads 24 along with an annular lower end 26 to which the ground electrode 18 is welded or otherwise attached. Similarly, all other components of the spark plug 10 (including those not shown) can be constructed using known techniques and materials, excepting of course the ground and/or center electrodes 16, 18 which are constructed with firing tip 20 and/or 22, as will be described below.

As is known, the annular end 26 of housing 12 defines an opening 28 through which insulator 14 protrudes. Center electrode 16 is permanently mounted within insulator 14 by a glass seal or using any other suitable technique. It extends out of insulator 14 through an exposed, axial end 30. Ground electrode 18 is in the form of a

WO 2006/008659

5

10

15

20

25

conventional ninety-degree elbow that is mechanically and electrically attached to housing 12 at one end 32 and that terminates opposite center electrode 16 at its other end 34. This free end 34 comprises a firing end of the ground electrode 18 that, along with the corresponding firing end of center electrode 16, defines a spark gap 36 therebetween.

The firing tips 20, 22 are each located at the firing ends of their respective electrodes 16, 18 so that they provide sparking surfaces for the emission and reception of electrons across the spark gap 36. These firing ends are shown in cross-section for purposes of illustrating the firing tips which, in this embodiment, comprise pads welded into place on the firing ends. As shown, the firing tips 20, 22 can be welded into partial recesses on each electrode. Optionally, one or both of the pads can be fully recessed on its associated electrode or can be welded onto an outer surface of the electrode without being recessed at all.

Each firing tip is formed from an alloy containing iridium, rhodium, tungsten, and zirconium. Preferably, the alloy is formed from a combination of iridium with 1-3 wt % rhodium, 0.1-0.5 wt % tungsten, and 0-0.5 wt % zirconium with no more than minor amounts of anything else. "Minor amounts," means a combined maximum of 2000 ppm of unspecified base metal and PGM (platinum group metals) impurities. Preferably, the amount of zirconium is kept to above 0.01 wt % (i.e., 0.01-0.05 wt %) and more preferably within the range of 0.01-0.04 wt % and, with either of these two zirconium ranges, preferably the rhodium is within the range of 1.5-2.5 wt % and the tungsten within the range of 0.25-0.35 wt %. In a highly preferred embodiment, the alloy is formed from about 2.0 wt % rhodium, about 0.3 wt % tungsten, about 0.02 wt % zirconium, and the balance iridium with no more than trace amounts of anything else. The alloy can be formed by known processes such as by melting the desired amounts of iridium, rhodium, tungsten, and zirconium together. After melting, the alloy can be converted into a powdered form by an atomization process, as is known to those skilled in the art. The powdered alloy can then be isostatically pressed into solid form, with secondary shaping operations being

10

15

20

30

used if necessary to achieve the desired final form. Techniques and procedures for accomplishing these steps are known to those skilled in the art.

Although the electrodes can be made directly from the alloy, preferably they are separately formed from a more conventional electrically-conductive material, with the alloy being formed into firing tips for subsequent attachment to the electrodes. Once both the firing tips and electrodes are formed, the firing tips are then permanently attached, both mechanically and electrically, to their associated electrodes by metallurgical bonding, such as laser welding, laser joining, or other suitable means. This results in the electrodes each having an integral firing tip that provides an exposed sparking surface for the electrode. Laser welding can be done according to any of a number of techniques well known to those skilled in the art. Laser joining involves forming a mechanical interlock of the electrode to the firing tip by using laser light to melt the electrode material so that it can flow into a recess or other surface feature of the firing tip, with the electrode thereafter being allowed to solidify and lock the firing tip in place. This laser joining technique is more fully described in European Patent Office publication no. EP 1 286 442 A1, the complete disclosure of which is hereby incorporated by reference.

As will be appreciated, the firing tips 20, 22 need not be pads, but can take the form of a rivet 40 (shown in Fig. 2), a wire 42 (shown in Fig. 3), a ball (not shown), or any other suitable shape. Although a round-end rivet is shown in Fig. 2, a rivet having a conical or frusto-conical head could also be used. As indicated in Fig. 3, the firing tip can, but need not, include one or more surface features such as grooves 44 to permit it to be interlocked to the electrode using the laser joining technique discussed above. The construction and mounting of these various types of firing tips is known to those skilled in the art. Also, although the firing ends of both the center and ground electrodes are shown having a firing tip formed iridium/rhodium/tungsten/zirconium alloy, it will be appreciated that the alloy could be used on only one of the electrodes. The other electrode can be utilized without any firing tip or can include a firing tip formed from another precious metal or precious metal alloy. For example, in one embodiment, the center electrode firing tip 20 can be

15

20

25

formed from the iridium/rhodium/tungsten/zirconium alloy and the ground electrode firing tip 20 can be formed from platinum or a platinum alloy.

As discussed in the inventors' prior published applications WO 2004/007782A1 and WO 2004/008596A2, the combination of iridium, rhodium, tungsten, and zirconium has been found to yield an alloy that exhibits good resistance to both spark and oxidative consumption, and the alloy disclosed in those published applications permits these benefits to be maintained using relatively small amounts of rhodium. In the present invention, the inventors have reduced the amount of rhodium from the specific formulations disclosed in those published applications, and this change would normally be expected to provide reduced performance in spark plug applications. However, testing has shown that unexpectedly, the alloy example disclosed herein using the same amount of tungsten, but with 2 wt % rhodium and 0.02 wt % zirconium provides as good as or marginally better spark plug electrode performance than the earlier formulations while exhibiting less tearing and cracking of the alloy during the metal forming operations used to shape the metal into a fine wire spark plug electrode. Thus, the present invention provides at least as good resistance to both spark and oxidative consumption, while providing improved workability when drawing and/or otherwise shaping it into a spark plug electrode.

It will thus be apparent that there has been provided in accordance with the present invention an ignition device and manufacturing method therefor which achieves the aims and advantages specified herein. It will, of course, be understood that the foregoing description is of preferred exemplary embodiments of the invention and that the invention is not limited to the specific embodiments shown. Various changes and modifications will become apparent to those skilled in the art. For example, although an ignition device in the form of a spark plug has been illustrated, it will be appreciated that the invention can be incorporated into an igniter of the type in which sparking occurs across the surface of a semiconducting material disposed between the center electrode and an annular ground electrode. All such changes and modifications are intended to be within the scope of the present invention.

10

15

20

CLAIMS

- 1. An ignition device (10) for an internal combustion engine, comprising: a housing (12);
- an insulator (14) secured within said housing (12) and having an exposed axial end (30) at an opening (28) in said housing;
- a center electrode (16) mounted in said insulator (14) and extending out of said insulator through said axial end (30); and
- a ground electrode (18) mounted on said housing (12) and terminating at a firing end (34) located opposite said center electrode (16) to define a spark gap (36) therebetween;

characterized in that at least one of said electrodes (16, 18) includes a firing tip (20, 22) formed from an alloy containing iridium, rhodium, tungsten, and zirconium, wherein the zirconium is included in an amount less than 0.05 wt %.

- 2. An ignition device as defined in claim 1, characterized in that said alloy is formed from a combination of iridium with 1-3 wt % rhodium, 0.1-0.5 wt % tungsten, and 0.01-0.05 wt % zirconium.
 - 3. An ignition device as defined in claim 1, characterized in that said alloy is formed from a combination of iridium with about 2 wt % rhodium, about 0.3 wt % tungsten, and about 0.02 wt % zirconium.
- 4. An ignition device as defined in claim 1, characterized in that said firing tip (20, 22) is metallurgically bonded to said center electrode (16) at said spark gap (36).
- 5. An ignition device as defined in claim 4, characterized in that said firing tip (20, 22) comprises a section of wire (42) laser joined to said center electrode (16).
- 6. An ignition device as defined in claim 4, characterized in that said firing end (34) of said ground electrode (18) includes a firing tip (22) located opposite the firing tip (20) of said center electrode (16).

- 7. An ignition device as defined in claim 6, characterized in that said firing tip (22) on said ground electrode (18) comprises platinum or a platinum alloy.
- 8. An ignition device as defined in claim 7, characterized in that said firing tip (20) on said center electrode (16) is formed from a combination of iridium with 1-3 wt % rhodium, 0.1-0.5 wt % tungsten, and 0.01-0.05 wt % zirconium.
- 9. An ignition device as defined in claim 7, characterized in that said firing tip (20) on said center electrode (16) is formed from a combination of iridium with about 2 wt % rhodium, about 0.3 wt % tungsten, and about 0.02 wt % zirconium.
- 10. An ignition device as defined in claim 1, characterized in that said ignition device comprises a spark plug (10).
 - 11. An ignition device as defined in claim 1, characterized in that said firing tip (20, 22) consists essentially of iridium, rhodium, tungsten, and zirconium.
 - 12. An ignition device as defined in claim 11, characterized in that both said electrodes (16, 18) include a firing tip (20, 22) consisting essentially of iridium, rhodium, tungsten, and zirconium.
 - 13. An ignition device as defined in claim 11, characterized in that said firing tip (20, 22) is made from an alloy that is formed from a combination of iridium with 1-3 wt % rhodium, 0.1-0.5 wt % tungsten, and 0.01-0.05 wt % zirconium.
- 14. An ignition device as defined in claim 11, characterized in that said firing tip (20, 22) is made from alloy that is formed from a combination of iridium with about 2 wt % rhodium, about 0.3 wt % tungsten, and about 0.02 wt % zirconium.
 - 15. A method of manufacturing an electrode (16, 18) for an ignition device (10) having a housing (12), a second electrode (18, 16), and an insulator (14) mounted

10

15

within the housing (12) to support and electrically isolate the two electrodes (16, 18), the method characterized by the steps of:

- (a) forming a firing tip (20, 22) from an alloy that includes iridium, rhodium, tungsten, and zirconium in an amount of 0.01-0.05 wt %,
- (b) forming an electrode (16, 18) from an electrically-conductive material other than said alloy, and
- (c) attaching said firing tip (20, 22) onto an end portion of said electrode (16, 18) to thereby provide said electrode with an integral firing tip that provides an exposed sparking surface for said electrode.
- 16. The method set forth in claim 15, characterized in that step (a) further comprises forming said firing tip (20, 22) from an alloy made from a combination of iridium with 1-3 wt % rhodium, 0.1-0.5 wt % tungsten, and 0.01-0.05 wt % zirconium.
 - 17. The method set forth in claim 15, characterized in that step (a) further comprises forming said firing tip (20, 22) from an alloy made from a combination of iridium with about 2 wt % rhodium, about 0.3 wt % tungsten, and about 0.02 wt % zirconium.
 - 18. The method set forth in claim 15, characterized in that step (a) further comprises forming said firing tip (20, 22) as a pad, rivet, ball or wire.
- 19. The method set forth in claim 15, characterized in that step (c) further comprises laser joining said firing tip (20, 22) onto an end face of a center electrode (16).
 - 20. The method set forth in claim 15, characterized in that step (c) further comprises attaching said firing tip (20, 22) onto an end portion of a ground electrode (18).
- 25 21. An ignition device (10) for an internal combustion engine, comprising: a housing (12);

an insulator (14) secured within said housing (12) and having an exposed axial end (30) at an opening (28) in said housing;

a center electrode (16) mounted in said insulator (14) and extending out of said insulator through said axial end (30); and

a ground electrode (18) mounted on said housing (12) and terminating at a firing end (34) located opposite said center electrode (16) to define a spark gap (36) therebetween;

characterized in that at least one of said electrodes (16, 18) includes a firing tip (20, 22) formed from an alloy containing iridium, 1-3 wt % rhodium, and zirconium, wherein the zirconium is included in an amount less than 0.05 wt %.

- 22. An ignition device as defined in claim 21, characterized in that said alloy includes 0.1-0.5 wt % tungsten.
- 23. An ignition device as defined in claim 21, characterized in that said alloy is formed from a combination of iridium with about 2 wt % rhodium, about 0.3 wt % tungsten, and about 0.02 wt % zirconium.
- 24. An ignition device as defined in claim 21, characterized in that said firing tip (20, 22) is laser joined to said center electrode (16).
- 25. An ignition device as defined in claim 24, characterized in that said ground electrode (18) includes a firing tip (22) formed from platinum or a platinum alloy.
- 26. An ignition device as defined in claim 21, characterized in that both said electrodes (16, 18) include a firing tip (20, 22) formed from said alloy.

1/1

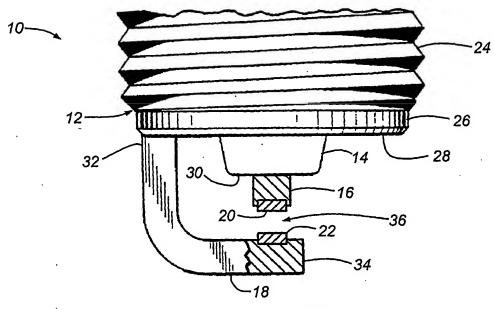
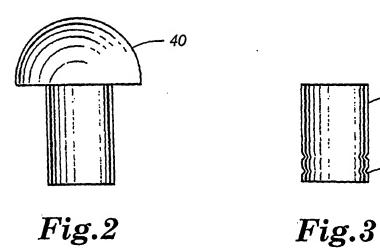


Fig.1



3/12/2007, EAST Version: 2.1.0.14